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310 Jesse Hall

Columbia, MO 65211 -1230

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14. ABSTRACT
This research addresses some of the challenges to developing improved combustion models for the discovery of alternative fuels for future engine design. We are performing studies of selected systems relevant to predicting the chemistry of fuels such as JP-8 and notional surrogates. The particular applications are chosen to facilitate the development of the methods and to contribute to understanding of the chemistry. There are two prime objectives of the research. One is to develop and apply efficient methods for using ab initio potential energy surfaces (PESs) computed with high levels electronic structure theory to predict rates of elementary reaction occurring in

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Report Title

Final Report: Ab Initio-Based Predictions of Hydrocarbon Combustion Chemistry

ABSTRACT

This research addresses some of the challenges to developing improved combustion models for the discovery of alternative fuels for future engine design. We are performing studies of selected systems relevant to predicting the chemistry of fuels such as JP-8 and notional surrogates. The particular applications are chosen to facilitate the development of the methods and to contribute to understanding of the chemistry. There are two prime objectives of the research. One is to develop and apply efficient methods for using ab initio potential energy surfaces (PESs) computed with high-levels electronic structure theory to predict rates of elementary reaction occurring in hydrocarbon combustion at normal and extreme conditions. We are developing efficient, robust methods for automatically generating accurate global PESs and for direct dynamics simulations using interpolating moving least squares (IMLS) that guarantee high fidelity to ab initio data. A particular focus of the research is the prediction of reaction rates at extreme conditions. Preliminary studies are being carried out using approximate PESs as we design ab initio-based PESs. We are developing a new approach for simulating reactions at high pressures and temperatures.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/20/2015	5.00	Luis A. Rivera-Rivera, Albert F. Wagner, Thomas D. Sewell, Donald L. Thompson. Pressure effects on the relaxation of an excited nitromethane molecule in an argon bath, The Journal of Chemical Physics, (01 2015): 0. doi: 10.1063/1.4904314
08/27/2013	1.00	Richard Dawes, Jamin W. Perry, Albert F. Wagner, Donald L. Thompson. A Classical Trajectory Study of the Intramolecular Dynamics, Isomerization, and Unimolecular Dissociation of HO2, J Chem Phys, (10 2013): 1. doi:
08/27/2013	2.00	Albert F. Wagner, Luis A. Rivera-Rivera, Damien Bachellerie, Jamin W. Perry, Donald L. Thompson. A Classical Trajectory Study of the Dissociation and Isomerization of C2H5, J Phys Chem A, (02 2013): 1. doi:
TOTAL:	**3**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Jeffrey D. Veals, Rezvan Chitsazi, Yi Shi, and Donald L. Thompson, "A Density Functional Theory and Ab Initio Study of Al + CO2 Reactions," Midwest Regional Meeting American Chemical Society, 12-15 November 2014, University of Missouri, Columbia, MO. [poster presentation]

2. Homayoon Rafatijo and Donald L. Thompson, "Predicting Reaction Pathways using Dynamical Mapping: Hydrogen Combustion," Midwest Regional Meeting American Chemical Society, 12-15 November 2014, University of Missouri, Columbia, MO. [poster presentation]

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

None.

Patents Awarded

Awards

None.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Yi Shi	0.63	
Rezvan Chitsazi	1.00	
FTE Equivalent:	**1.63**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Manuel Monge Palacios	0.38
FTE Equivalent:	**0.38**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Ezekiel Piskulich	0.69	Physics
FTE Equivalent:	**0.69**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

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Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

None.

Final Report
Grant # W911NF-09-1-0199

Ab Initio-Based Predictions of Hydrocarbon Combustion Chemistry

PI: **Donald L. Thompson**
Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211

Overview. The practical objective of the research was to address some of the challenges to developing improved hydrocarbon combustion models. This requires new theoretical and computational methods for predicting reaction rates, particularly for extreme pressures. We have developed and applied a novel approach for computing the effects of pressure on reactions and relaxation of radicals and molecules, which we have used in studies of the relaxation of excited species in an Ar bath. This method allows us to avoid (and evaluate) the usual assumption of bimolecular collisions, which breaks down at high pressures. For predictability we need to develop efficient methods for using *ab initio* potential energy surfaces (PESs) computed with high levels of quantum chemistry theory to provide accurate rates of elementary reactions. The methods all make use of classical molecular dynamics.

The Influence of Pressure on the Relaxation of Excited Radicals and Molecules. A major thrust of the research was on the effects of pressure on the relaxation of excited species in the gas phase. Our main interest was to explore ranges of pressure where the relaxation occurs primarily in "isolated" bimolecular collisions to levels where the bimolecular in no longer valid. The relaxation of radicals and molecules is usually assumed to occur in collisions of the excited species with a single other species. Clearly this bimolecular mechanism must cease to be valid at extremely high pressures. Our interest was to determine the change from the bimolecular process to relaxation processes in which more than one other molecule or radical in involved.

Molecular dynamics simulation of the relaxation of three different species (CH_3NO_2, HO_2, and OH) in an argon bath gas at pressures over the range 10 atm to 400 atm and at temperatures of 300 K (CH_3NO_2 and OH) or 800 K (HO_2) were carried out. The three species were chosen for their considerable differences in size, and molecular and vibrational structures. Acceptably accurate intramolecular potential energy surfaces were available for all three. The interactions of CH_3NO_2 and HO_2 with Ar were approximated by pairwise additive Buckingham (exp-6) potentials with the atoms in the excited species treated as the nearest rage gas, and the parameters determined by using combination rules and parameter values available in the literature; which has been shown to provide reasonably accurate intermolecular forces between molecules and radicals. The Ar-H interaction in OH was represented by the Lennard-Jones potential and the Ar-O as in the other species, that is, with the exp-6.

Classical molecular dynamics simulations were carried out for 1000 Ar atoms and one initially excited species in a cell with periodic boundary conditions. The molecule or radical was instantaneously excited by either statistically distributing energy among the internal degrees of freedom (50 kcal/mol for CH_3NO_2 and 45 kcal/mol for HO_2), but in the case of OH the relaxation of the specific state v=2, J=0 was studied. The translational energies of the excited species and Ar atoms were selected from the Maxwell-Boltzmann distribution.

A comparison of the relative decay rates for rotation and vibration at substantial pressure is shown in Fig. 1 for the three systems. In all three cases, as expected, rotational relaxation is one to ten orders of magnitude faster than vibrational relaxation. The results clearly show the

equilibration of the rotational energy to values approaching 1.5kT for CH_3NO_2 and HO_2 (~0.9 kcal/mol (T = 300 K) and ~2.4 kcal/mol (T = 800 K), respectively, and kT for OH (~0.6 kcal/mol). However, the vibrational relaxation rates vary among the three systems by at least an order of magnitude; the rate for CH_3NO_2 is the fastest and for OH by far the slowest. This variation in relaxation is likely due to the different types of vibrational motion possible in these species; for example, CH_3NO_2 has a low frequency hindered rotor that can couple well with the motions of the bath gas atoms.

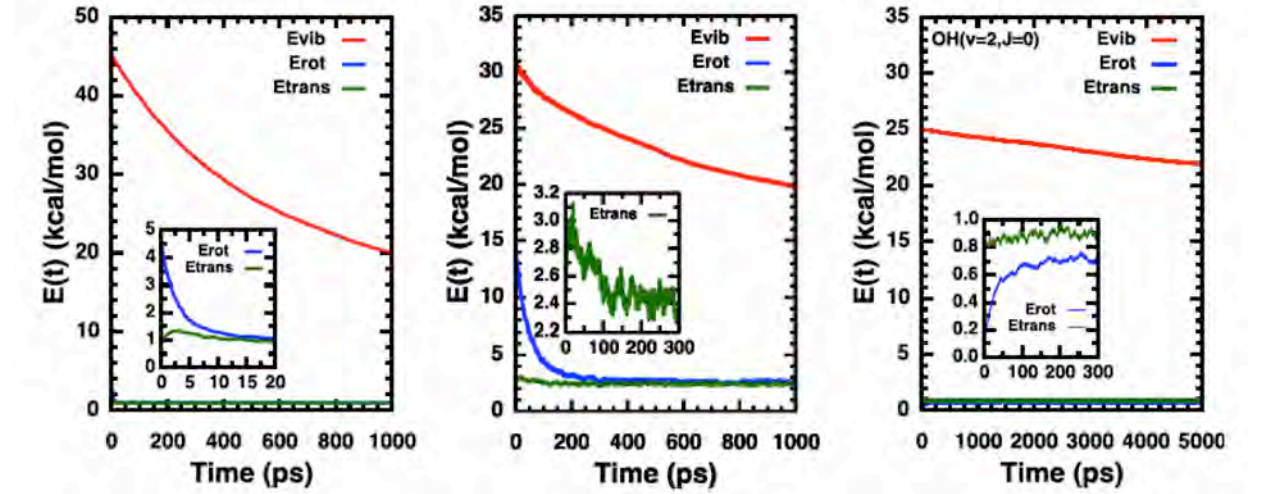


Figure 1: The ensemble averaged vibrational energy (in red), rotational energy (in blue), and translational energy (in green) as a function of time for CH_3NO_2 in a (300K, 100 atm) Ar bath (left), for HO_2 in a (800K, 100 atm) Ar bath (middle), and OH in a (300K, 50 atm) Ar bath (right).

Figure 2 shows the normalized excess vibrational energy $E_{nrm\text{-}vib}(t)$ for all the simulations.

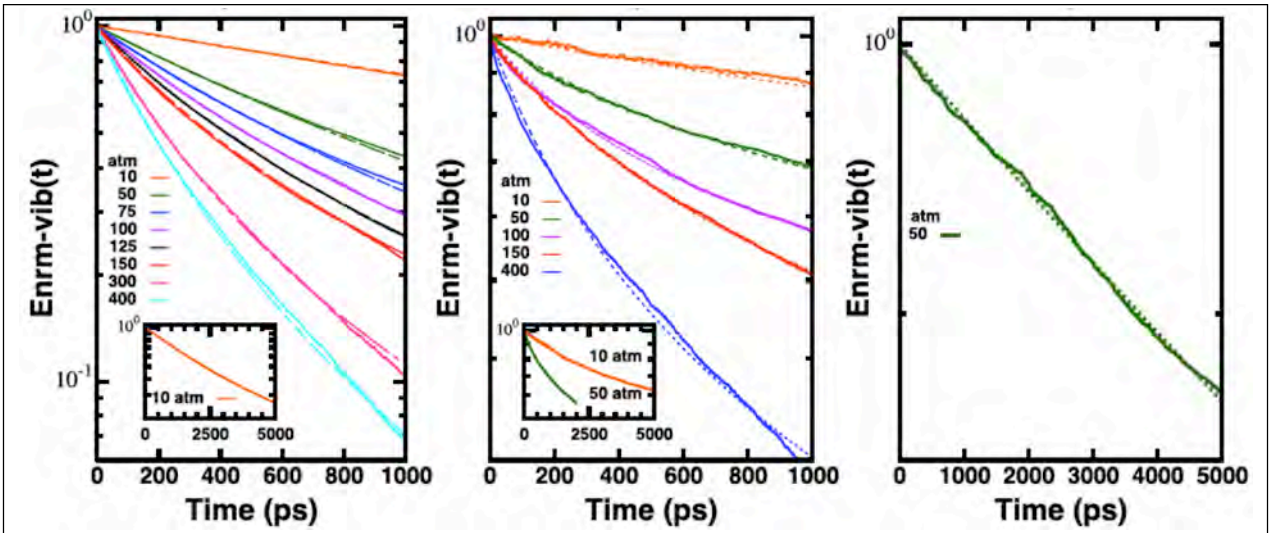


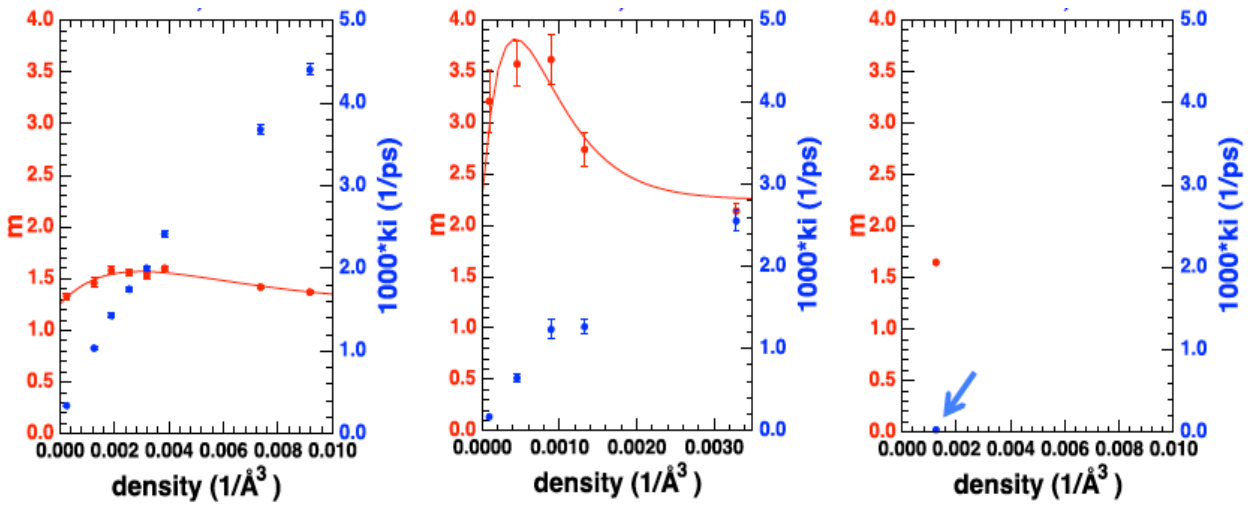
Figure 2. The normalized excess vibrational energy (see text) as a function of time for CH_3NO_2 in a 300K Ar bath gas at eight pressures (left), for HO_2 in a 800K Ar bath gas at five pressures (middle), and for OH (v=2,J=0) in a 300K Ar bath gas at one pressure. The solid lines are the simulation results while the broken lines are the LS fit (see text).

$E_{nrm\text{-}vib}(t)$, the vibrational energy above the thermal vibrational energy, is plotted as a function of time, including the temperature increase of the bath gas due to molecular energy lost from the initially excited molecule up to that time. The results are normalized to the excess energy appropriate to the initial absolute value of the energy. The normalization allows the different systems and pressures to be conveniently compared. The dashed curves in Fig. 2 are fits of the trajectory results to the Lendvay and Schatz (LS) [G. Lendvay and G. C. Schatz, J. Phys. Chem. **95**, 8748 (1991).] equation:

$$\frac{E(t)}{E(0)} \equiv E_{nrm}(t) = \left[1-(1-m)k_i t\right]^{\frac{1}{1-m}}.$$

This functional form for the decay of the normalized energy $E_{nrm}(t)$ has the virtue that it involves only *two* parameters, and each parameter responds to different temporal regions of the decay. At t=0, the k_i parameter equals dE_{nrm}/dt, the initial rate of decay. To the extent that this form is appropriate, k_i will be determined primarily by the early behavior of the decay curve. The parameter m determines curvature. When m = 1, Eq. (1) can be shown to collapse to a single exponential function with rate k_i. For $m > 1$, $E_{nrm}(t)$ rises up from the single-exponential straight-line behavior on a semi-log plot, indicating that as excitation level of the species decreases the relaxation rate decreases. For $m < 1$ (including negative values), $E_{nrm}(t)$ curves down from single-exponential (linear) behavior, indicating that as excitation level decreases the relaxation rate increases. Figure 2 shows positive curvature at all pressures. For the lowest pressure, 10 atm, it appears that a single decay rate applies over 1000 ps for CH_3NO_2 and HO_2; however, as the results in the inset show, when the process is followed for 5000 ps, there is clearly positive curvature. While the LS functional form fits the results quite well, we see it as merely an empirical fit without a theoretical basis or justification. We were unsuccessful in finding a physical explanation for bi-exponential behavior, something that has long been observed, used in modeling of combustion and other complex processes, yet never shown to be more than an empirical fitting function.

Figure 3. The optimized values of m (in red and corresponding to the red axis) and k_i (in blue and corresponding to the blue axis) as functions of density. The values are from fits to the LS equation, shown in Fig. 2. The densities correspond to the pressures in Fig. 2.



Plots of the parameter values m and k_i as functions of density are shown in Fig. 3. The density is determined by the size of the periodic box in the simulations at each pressure and temperature (this accounts for any deviation at higher pressures from the ideal gas law). The different density scale for HO_2 reflects the fact that at nearly three times the temperature, density over the same pressure range is about 1/3 less.

As one can see from the red points and curves in Fig. 3 there is positive curvature in all cases with the HO_2 curve considerably more curved than that for the other two systems. The solid curve in Fig. 3 is a fit of the density dependence of m to the functional form $a + b\rho e^{-c\rho}$, where ρ is the density. This fit shows that while both CH_3NO_2 and HO_2 show some pressure dependence to m, the m values lie in a relatively narrow band. The persistence of this band of curvature over such a wide variation of conditions suggests that the internal structure of molecule is involved in the relaxation process. For OH, the simplicity of this internal structure permits a deeper interpretation of the origin of curvature. OH has only one vibrational degree of freedom and Fig. 1 shows that only minor amounts of vibrational-rotational coupling occur for the initial OH state of (v=2,J=0). One can then model the vibrational energy decay in terms of decay rates from specific vibrational levels and obtain an analytic solution. Because the energy gap between OH vibrational levels is so large (3737 cm^{-1} fundamental frequency), the only substantial rates are downward rates to adjacent levels, *i.e.*, $k_{v,v-1}$ where v is the vibrational quantum number of the initial state. From perturbation theory for harmonic oscillators, it is well know that $k_{v,v-1}$ is proportional to v. In other words, as energy leaks out of OH in to the bath gas, the increasing populations in lower OH vibrational levels experience slower rates of further de-excitation. Nonetheless, substitution of $k_{v,v-1} = vk_{10}$ into the analytic solution produces a single exponential decay (m = 1) given by k_{10}. The only way to get m > 1 is for $k_{v,v-1} > vk_{10}$. This can be achieved by recognizing that anharmonicity of the vibrational levels causes the energy gap between adjacent levels to decrease as the energy of the oscillator increases. Kohno *et al*. [N. Kohno, J. Yamashita, C. Kadochiku, H. Kohguchi, and K. Yamasaki, J. Phys. Chem. A **117**, 3253 (2013).] in an OH/He single collision experimental study observed that $k_{v,v-1}/v$ depended exponentially on the anharmonic energy gap. Inserting an exponential-gap dependence in the analytic kinetics model produces positive curvature, as is found in the simulations. This suggests that the positive curvature present in all the results in Fig. 2 are due at least in part to the reduced effects of anharmonicity at lower internal energies within the three molecules.

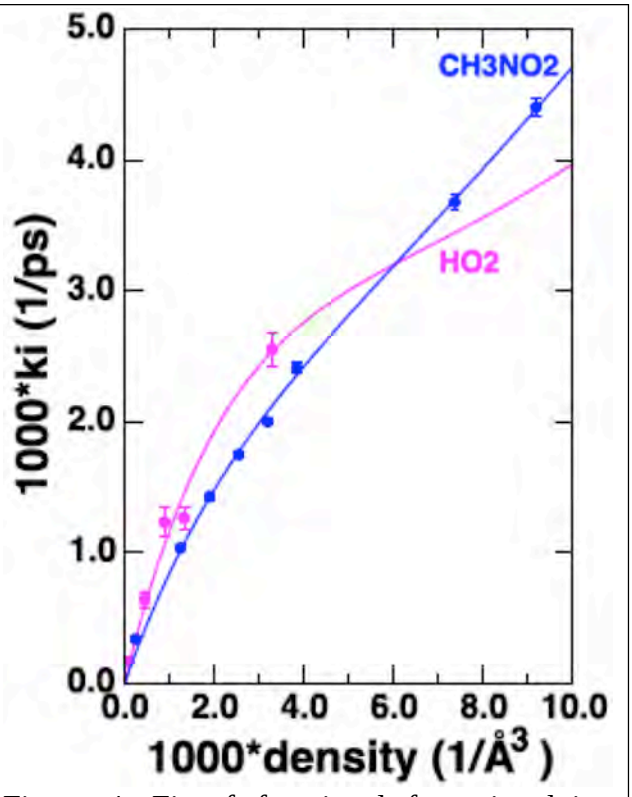


Figure 4. Fit of functional form involving multiple collisions to the density dependent k_i values of Fig. 3.

The results in Fig. 3 show that the k_i parameter assumes values that increase monotonically over the factor of ~40 variation in the density for both CH_3NO_2 and HO_2. However, the results in the figure also clearly show that k_i is *not* directly proportional to density over the entire interval. At a pressure of ~100 atm (density ~0.002 $Å^{-3}$ for CH_3NO_2 and ~0.001 $Å^{-3}$ for HO_2), k_i begins to drop below what is expected from a direct proportionality. Recall that k_i is the relaxation rate at t=0 for the LS fit. The initial conditions of the molecule and radical are statistically identical for all densities. This implies that the loss of direct proportionality is a consequence of a change in the nature of the interaction of Ar bath with the excited species as a function of density. The solid curve in Fig. 4 is a fit of the density dependence of k_i to the functional form

$$k_i = P_\rho(1)\rho k_1 + \sum_{L>1} P_\rho(L)\,\rho(Lk_2),$$

where ρ is the density and $P_\rho(L)$ is the normalized probability of having L atoms colliding simultaneously with the molecule, and k_1 and k_2 are adjustable molecular relaxation rates per Ar colliding atom. A simple combinatorial model based on the size of the molecule and the size of the Ar atom leads to an analytic expression for $P_\rho(L)$ and suggests that at the highest pressure (400 atm) single collisions are rare and simultaneous collisions involving ~5 Ar atoms is the norm. Roll-off of the initial rate from the low-density extrapolation occurs because the rate for collision events with L Ar atoms grows with L more slowly than L times the rate for collision events with one Ar atom.

The relaxation of normalized excess rotational energy can be analyzed with the LS fit in a manner similar to Fig. 2 for CH_3NO_2 and HO_2. The resulting m and k_i parameters are plotted in Fig. 5 in a manner similar to Fig. 3 for vibrational energy. There are two significant differences between Fig. 5 for rotational energy and Fig. 3 for vibrational energy. First, the m values for rotation are relatively similar for the two species but a factor of two different for vibration. Second, for both species the rotational k_i is directly proportional to density over the interval of simulated densities; the deviation from direct proportionality at higher pressures does not occur. The reason for this is the subject of on-going study.

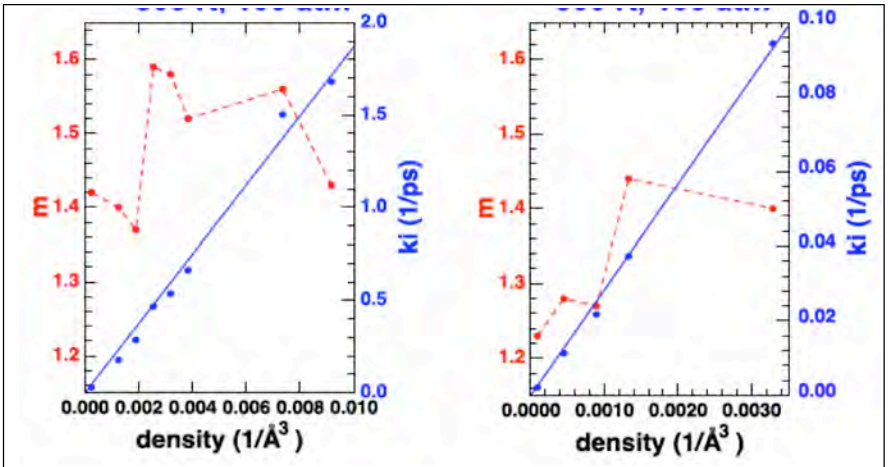


Figure 5. The optimized value of m (in red and corresponding to the red axis) and k_i (in blue and corresponding to the blue axis) as a function of density for LS fits to normalized excess rotational energy. The CH_3NO_2 results (left) and the HO_2 results (right) have densities corresponding to the pressures listed in Fig. 2.

This work provides further insight into the influence of increasing pressure on relaxation of internally excited species, however, it is clear that a full understanding will require further study. The present study shows the breakdown in the bimolecular collision assumption, but does not

provide sufficient knowledge of the mechanisms to allow us to explain the bi-exponential behavior of the decay rates. Thus, while we have advanced our understanding of pressure effects, further work is needed to achieve sufficient knowledge of the effects to either devise empirical relationships with wide applicability (e.g., to cover the many species involved in combustion) or to have a satisfactory theoretical (including mathematical) model.

Accurate PESs. Our initial focus was on the development of *ab initio*-based PESs for use in MD simulations of reactions. We began by considering the lower cost electronic structure methods for C_2H_5. We first investigated empirical potentials especially designed for the study of hydrocarbon systems, namely Reaxff and AIREBO. Both are cheap to compute and are close to acceptable accuracy for C_2H_5. We also examined Density functional theory (DFT), which are quickly being improved. Some give results comparable to commonly used *ab initio* methods at considerably lower computational cost. We tested the commonly used functionals B3LYP, PBE, and PW91; and found them not to be sufficiently accurate. We found that using the aug-cc-pVTZ basis set that the MO5 functional gives acceptable results. We are currently using the MO6, which is presumably more accurate than MO5, to develop automatic procedures for generating global PESs and for performing direct dynamics simulations. We also carried out direct dynamics simulations of the C_2H_5 dissociation and isomerization using DFT MO5-2X/CBSB7. The isomerization and dissociation reaction barriers are almost the same height, thus a good test case. Direct dynamics simulations for a system of this size with the high accuracy we require are expensive. The average propagation time for a trajectory at 150 kcal/mol is about two weeks. While this makes the calculations feasible (for this size radical) with the use of clusters, we wish to lower the computational cost. We will continue exploring ways of significantly reducing the cpu time for these kinds of calculations.

We have also searched for suitable reference potentials that we can use within a strategy we developed a few years ago in which we fit the difference between an approximate PES and *ab initio* data. The motivation for this approach is that the difference can be considerably "flatter" than the actual potential, thus requiring many fewer *ab initio* points for an accurate representation of the *ab initio* PES. our focus has been on C_2H_5. We have investigated ReaxFF and AIREBO. Both are cheap to compute and are close to acceptable accuracy for C_2H_5. We have used the aug-cc-pVTZ basis set with the MO5 functional to generate 10,000 data points for checking out fitting scheme. If an effective practical method is applicable to this radical it could be used for other larger systems. The isomerization (the transfer of a H-atom from the CH_3 end to the CH_2 end) and dissociation reaction barriers are almost the same height. These competitive reaction channels represent an interesting fundamental problem about which little is known, thus we have, as we work to develop the IMLS-based methods, also made a study of the effects of isomerization on dissociation. Knowing how such an isomerization affects the rate of dissociation could provide insights; for example, different energy distributions in products that might affect their subsequent chemistry.

This work has been published in J. Phys. Chem. A, and is available on the web (DOI: 10.1021/jp3099889): Albert Wagner, Luis A Rivera-Rivera, Damien Bachellerie, Jamin W Perry, and Donald L Thompson, "A Classical Trajectory Study of the Dissociation and Isomerization of C_2H_5." The abstract follows.

Abstract: Motivated by photo-dissociation experiments on the ethyl radical, we have performed a classical trajectory study of the dissociation and isomerization of C_2H_5 out to

100 ps over the energy range 100 to 150 kcal/mol. We used a customized version of AIREBO semi-empirical potential [Stuart *et al*. *J. Chem. Phys.* **112**, 6472 (2000)] for C_2H_5. The trajectory results were fit to a kinetics model of isomerization/dissociation competition and the model in turn was used to project results to the time scales of the experiments (~100 ns), and to test for evidence of incomplete mode-mixing in phase space. This analysis shows that there is incomplete mode mixing with the AIREBO potential at the upper end of our energy range, resulting in isomer population decay that is poly-exponential and in dissociation and isomerization rates that change with the number of isomerizations that have occurred. At the lower end of our energy range, isomer population decay is well described by a single exponential with isomerization and dissociation rates that are independent of the number of isomerization. No evidence was found for an extremely slow, non-RRKM dissociation process suggested by two experimental studies. The fraction of energy deposited in translational motion of the products is consistent with previous theoretical results of others but noticeably lower than the experimental studies. Also in contrast to the experimental and theoretical studies of others, these trajectory studies show non-negligible isotopic scrambling throughout our energy range due to some isomerization before dissociation in CH_3CD_2. The trajectory results support the assumption that at these energies an H or a D atom is equally likely to dissociate from the mixed-isotope methyl end of the molecule. We have also carried out direct dynamics simulations for C_2H_5 using the DFT method M05 with the 6-31+G(d,p) basis set for total energies 150, 200, and 250 kcal/mol. These calculations are the preliminary step in exploring ways to facilitate direct dynamics with interpolations to decrease the number of electronic structure calculations.

The intramolecular dynamics and unimolecular dissociation of isolated HO_2: We have carried out studies of intramolecular vibrational energy transfer, isomerization, and dissociation of HO_2 using highly accurate PESs fit to high-level electronic structure theory results. All the previous theoretical studies of the radical were done using approximate PESs, and most focused primarily on it as a collision complex in reactions of H + O_2 and OH + O. We needed to develop a better knowledge of the dynamics of the radical as a foundation for interpreting our results for pressure effects. Our results show that there are mode-specific effects in both the intramolecular energy transfer and unimolecular dissociation because the O-O and O-H vibrational modes are weakly coupled. These results, based on highly accurate PESs, are in conflict with conclusions of the previous theoretical studies that had been carried out using an approximate PES. They also illustrate the need to develop more effective ways of using high-level electronic structure theory in predicting vibrational relaxation and chemical reactions.

The intramolecular dynamics and unimolecular dissociation of isolated HO_2: We have carried out studies of intramolecular vibrational energy transfer (IVR), isomerization, and dissociation of HO_2 using highly accurate PESs fit to high-level electronic structure theory results. All the previous theoretical studies of the radical were done using approximate PESs, and most focused primarily on it as a collision complex in reactions of H + O_2 and OH + O. We needed to develop a better knowledge of the dynamics of the radical as a foundation for interpreting our results for pressure effects. Our results show that there are mode-specific effects in both the intramolecular energy transfer and unimolecular dissociation because the O-O and O-H vibrational modes are weakly coupled. These results, based on highly accurate PESs, are in conflict with conclusions of the previous theoretical

studies that had been carried out using an approximate PES. The results also illustrate the need to develop more effective ways of using high-level electronic structure theory in predicting vibrational relaxation and chemical reactions.

We have published a study of molecular dynamics simulations of this important combustion radical using highly accurate PESs based on high-level electronic structure theory results. The study has been published: Jamin W. Perry, Richard Dawes, Albert F. Wagner, and Donald L. Thompson, "A Classical Trajectory Study of the Intramolecular Dynamics, Isomerization, and Unimolecular Dissociation of HO_2," J. Chem. Phys. **139**, 084319 (2013); http://dx.doi.org/10.1063/1.4818879); the abstract follows:

Abstract: The classical dynamics and rates of isomerization and dissociation of HO_2 have been studied using two potential energy surfaces (PESs) based on interpolative fittings of *ab initio* data: An interpolative moving least-squares (IMLS) surface [A. Li, D. Xie, R. Dawes, A. W. Jasper, J. Ma, and H. Guo, J. Chem. Phys. 133 , 144306 (2010)] and the cubic-spline-fitted PES reported by Xu, Xie, Zhang, Lin, and Guo (XXZLG) [J. Chem. Phys. 127, 024304 (2007)]. Both PESs are based on similar, though not identical, internally contracted multi-reference configuration interaction with Davidson correction (icMRCI**+**Q) electronic structure calculations; the IMLS PES includes complete basis set (CBS) extrapolation. The coordinate range of the IMLS PES is limited to non-reactive processes. Surfaces-of-section show similar generally regular phase space structures for the IMLS and XXZLG PESs with increasing energy. The intramolecular vibrational energy redistribution (IVR) at energies above and below the threshold of isomerization is slow, especially for O–O stretch excitations, consistent with the regularity in the surfaces-of-section. The slow IVR rates lead to mode-specific effects that are prominent for isomerization (on both the IMLS and XXZLG) and modest for unimolecular dissociation to H **+** O_2 (accessible only on the XXZLG PES). Even with statistical distributions of initial energy, slow IVR rates result in double exponential decay for isomerization, with the slower rate correlated with slow IVR rates for O–O vibrational excitation. The IVR and isomerization rates computed for the IMLS and XXZLG PESs are quantitatively, but not qualitatively, different from one another with the largest differences ascribed to the ~ 2 kcal/mol difference in the isomerization barrier heights. The IMLS and XXZLG results are compared with those obtained using the global, semi-empirical double many-body expansion DMBE-IV PES [M. R. Pastrana, L. A. M. Quintales, J. Brandão, and A. J. C. Varandas, J. Chem. Phys. 94, 8073 (1990)], for which the surfaces-of-section display more irregular phase space structure, much faster IVR rates, and significantly less mode-specific effects in isomerization and unimolecular dissociation. The calculated IVR results for all three PESs are reasonably well represented by an analytic, coupled three-mode energy transfer model.

Current Status on Improving *ab initio* PES fitting and direct dynamics. In earlier work, we developed reliable, highly accurate methods for fitting high-level electronic structure theory results for up to six dimensions (four atoms). In this grant we have explored ways to speed up the interpolations to obtain gradients sufficiently fast to make IMLS more practical for larger systems. The cost of evaluations (interpolations) for high-order basis functions can be prohibitively expensive in cpu time, thus limiting their use as presently formulated in classical trajectory calculations. We considered ways to do this for IMLS-directed global PES construction, in trajectory-generated IMLS PESs, and in IMLS-assisted direct dynamics. We note however that the IMLS method, as now formulated, still requires far too much cpu time for evaluations of energies (and gradients) for effective use MD simulations of large systems. We

have shown (in earlier studies) IMLS to be a powerful method for use in predictions of vibrational spectroscopy where far fewer energy points are needed. We remain interested in exploring ways to make better use of high-level *ab initio* results, and thus will continue the work begun in this grant. Clearly innovation is needed in interpolation methods, and other approaches need to be considered. Another, perhaps more promising, approach will be improved functionals for DFT. We have also carried out direct dynamics simulations for C_2H_5 using the DFT method M05 with the 6-31+G(d,p) basis set for total energies 150, 200, and 250 kcal/mol.

Atomic-level simulations of shock tubes: We have developed C++ codes for the direct atomic-level simulation of a shock tube. The purpose is to directly simulate the evolution of the lead shock and secondary waves in the shock tube, including the effects of reflections at the ends of the tube (*e.g.*, re-shocking of the driven gas, which is what leads to the high temperatures in shock tubes), and to simulate the excitation and subsequent relaxation of the N_2 molecules. In our initial simulations, the shock tube contained 40,000 He atoms as the driver and a 10% mole ratio solution of N_2 in Ar as the driven gas of 55,000 atoms. The initial temperature of the system was 298 K. The overall simulation cell was non-periodic along the length of the shock tube but periodic in the transverse directions; 5070 Å × 198 Å × 198 A (*i.e.*, ~0.5 micron length along the shock tube). The excitation and relaxation of N_2 are being studied in detail in terms of fundamental physical properties including translational energy, molecular angular momentum, and internal energy. The analysis is non-trivial because the system is non-steady in any reference frame; the local thermodynamic conditions under which the N_2 excitation and relaxation occurs vary along the length of the shock tube. Calculations and analyses are continuing. We anticipate writing a manuscript for publication in the next few months.